

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>5</sup> : B41J 2/21, B41M 5/00, C09D 11/02</p>	<p>A1</p>	<p>(11) International Publication Number: WO 95/00340 (43) International Publication Date: 5 January 1995 (05.01.95)</p>
<p>(21) International Application Number: PCT/US94/06815 (22) International Filing Date: 16 June 1994 (16.06.94) (30) Priority Data: 08/078,114 18 June 1993 (18.06.93) US (71) Applicant: REXHAM GRAPHICS INC. [US/US]; 28 Gaylord Street, South Hadley, MA 01075 (US). (72) Inventor: ANDERSON, Brian, L.; 77 Lambert Terrace, Chicopee, MA 01020 (US). (74) Agent: GESS, E., Joseph; Burns, Doane, Swecker &amp; Mathis, Washington and Prince Streets, P.O. Box 1404, Alexandria, VA 22313-1404 (US).</p>	<p>(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LU, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent: (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>	
<p>(54) Title: INK JET RECEIVER SHEET</p> <p>(57) Abstract</p> <p>Provided by the present invention is an ink jet receiver sheet comprised of a substrate and a coating containing a modified polyvinyl alcohol. The substrate is preferably paper based, and the modified polyvinyl alcohol is preferably carboxylated, acetoacetylated or modified with sulfonic acid. The use of modified polyvinyl alcohols in accordance with the present invention work very well with the class of ink jet inks that contain a cosolvent comprised of a polyol of at least three hydroxy groups or an amido functional cosolvent such as pyrrolidone. With the modified polyvinyl alcohol, the ink is found to spread upon contact with the surface and provide good print quality and good dry times.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

INK JET RECEIVER SHEETBACKGROUND OF THE INVENTION

The present invention relates to an ink jet receiver sheet for use in an ink jet recording process. More particularly, the present invention relates to an ink jet receiver sheet useful with ink jet inks containing amido functional cosolvents or polyol cosolvents having at least 3 hydroxy groups.

5 Ink jet printing inks for desktop, engineering, and graphic arts applications have changed dramatically over the past few years. When ink jet printers first appeared for desktop use in the early 1980s, many of the inks contained a high concentration, e.g., up to 60 weight percent, of a cosolvent, usually a glycol, to prevent clogging of the ink heads. With the advent of head cleaning stations on the printers, the need for the higher  
10 concentration of cosolvents was reduced.

With the development of the newer generation of ink jet printers, there has been a major shift in the ink formulations as well. The trend now is to use an ink that will perform adequately on plain paper in full color. The new ink formulations generally contain lower levels of cosolvents and contain polyols having at least 3 hydroxy groups as cosolvents or  
15 amido functional cosolvents such as pyrrolidone. These cosolvents have enhanced solubilizing strength for dyes, dispersing and wetting strength for ink pigments, and other solvent properties desirable for ink jet inks at lower solvent concentrations than previously used. This shift in the formulation and the presence of these cosolvents can have a great effect on the receptivity of the inks by the receiver sheet. Ink coalescence, beading and poor  
20 dry times can be the result of poor receptivity.

The use of a coated receiver sheet to enhance the receptivity of the ink is well known to the ink jet industry. For example, the use of polyvinyl alcohol in the ink receiving layer of an ink jet recording sheet is well known.

U.S. Patent No. 4,801,497 discloses a recording medium which comprises an ink  
25 receiving layer containing a cationically modified product of polyvinyl alcohol and a water-soluble polymer having no active hydrogen. The cationically modified product of polyvinyl alcohol is characterized as having a cationic group such as a primary to tertiary amino group or a quaternary ammonium salt group in a main chain or a side chain. The water-soluble polymer can be, for example, polyvinyl pyrrolidone.

-2-

U.S. Patent No. 4,503,111 discloses the use of a mixture of polyvinyl alcohol and polyvinyl pyrrolidone for the formation of an ink receiving layer. The mixture of polyvinyl alcohol and polyvinyl pyrrolidone is in the ratio of 3/1 to 1/3. Similarly, U.S. Patent No. 4,686,118 describes a recording medium useful in ink jet recording comprised of a substrate  
5 and an ink receiving layer thereon. The ink receiving layer is comprised of a mixture of polymers, with the first polymer having a number of hydroxyl groups, carboxyl groups or amino groups. One of the preferred polymers is polyvinyl alcohol. A second polymer is preferably a polymer not having a number of hydroxyl groups in a side chain, with such a polymer being polyvinyl pyrrolidone.

10 U.S. Patent No. 4,592,951 discloses an ink jet recording sheet comprised of a transparent support carrying a layer of a crosslinked polyvinyl alcohol. The crosslinking of the polyvinyl alcohol is carried out by treating the polyvinyl alcohol with a conventional crosslinking agent, such as a boron compound. Suitable boron compounds mentioned include boric acid, methyl borate, boron trifluoride, boric anhydride, pyroborates, peroxoborates and  
15 boranes. The transparent support can be any suitable transparent polymer material such as polymethacrylic acid, polyamides such as nylons, polyesters such as polymeric films derived from ethylene glycol terephthalic acid, polymeric cellulose derivatives, polycarbonates and polystyrene.

U.S. Patent No. 4,474,850 discloses a recording sheet for use in an ink jet recording  
20 process which is comprised of a transparent resin base and a coating thereon. The transparent resin base can be any suitable base such as polyester, polystyrene, polyvinyl chloride, polymethylmethacrylate, cellulose acetate and the like. The coating is comprised of a carboxylated, high molecular weight polymer or copolymer, and salts thereof. Particular monomers useful in formulating the polymer are disclosed as being acrylic or methacrylic  
25 acid, and esters thereof; vinyl acetates; or styrenated acrylics. The polymer may also contain other substituents in addition to carboxyl groups, such as hydroxyl, ester and amino groups.

European Patent Publication 0487350 discloses a receiver sheet comprised of a substrate and a coating. The coating is comprised of a pigment in a binder comprising  
30 polyvinyl alcohol and an additional binder component. The substrate may also be a transparency.

In more recent years, particular emphasis has been made on the use of paper as a substrate for an ink jet receiver sheet. Papers coated with materials compatible with ink jet

-3-

inks are known. For example, U.S. Patent No. 4,478,910 discloses an ink jet recording paper comprising a base sheet with a coating layer comprising a water-soluble polymeric binder and fine silica particles. The polymeric binder may include polyvinyl alcohol or its derivatives, water-soluble cellulose derivatives, water-soluble polymeric substances such as

5 polyvinyl pyrrolidone, or the like.

U.S. Patent No. 4,758,461 discloses a recording paper suitable for ink jet printing comprising a fibrous substrate paper on the surface of which a silicon containing type pigment and a fibrous material of the substrate paper are present in a mixed state. The paper can also contain an aqueous binder such as one or a mixture of two or more water-soluble or

10 water-dispersed polymers such as polyvinyl alcohol, starch, oxidized starch, cationized starch, casein, carboxymethyl cellulose, gelatin, hydroxyethyl cellulose, SBR latex, MBR latex, vinyl acetate emulsion, and the like.

U.S. Patent No. 4,780,356 discloses a recording sheet suitable for ink jet printing comprising a sheet of paper and porous particles on the paper surface. The particles can be

15 coated on a paper surface by means of a binder such as polyvinyl alcohol.

U.S. Patent No. 4,474,847 discloses a coated base paper for use in an ink jet recording process wherein the coating comprises a pigment and/or filler of non-flake structure and a binding agent dried on the paper. The pigment content is at least about 90 percent by weight of the dried coating, and the binding agent is predominantly hydrophilic.

U.S. Patent No. 4,686,118 discloses a recording medium having an ink receiving layer provided on a substrate. The ink receiving layer comprises at least a mixture of a polymer capable of forming intermolecular hydrogen bonds and a polymer incapable of forming intermolecular hydrogen bonds. The substrate can be opaque, e.g., paper, wood,

20 metal plate, or transparent, e.g., polyester film.

U.S. Patent No. 4,554,181 discloses an ink jet recording sheet having a recording surface which includes a combination of a water soluble polyvalent metal salt and a cationic polymer, said polymer having cationic groups which are available in the recording surface for insolubilizing an anionic dye.

25

U.S. Patent No. 4,617,239 discloses a method of coating paper to improve its surface

30 strength and printability by applying to the paper a silicon-containing modified polyvinyl alcohol agent or its saponification product. The coating agent forms a film on the surface of the paper which minimizes the penetration of the coating into the paper and improves the surface strength and printability of the paper. The coating agent may be incorporated with

-4-

other coating compounds, including synthetic resin emulsions such as styrene-butadiene latex, polyacrylate ester emulsion, polyvinyl acetate emulsion, vinyl acetate-acrylate ester copolymer emulsion, and vinyl acetate-ethylene copolymer emulsion. Further, the coating agent may be incorporated with pigments such as clay, calcium carbonate, titanium dioxide, 5 satin white, zinc oxide, silica, aluminum oxide, and cadmium sulfide.

There is a need in the ink jet industry, however, to provide an ink jet receiver sheet for the newer inks containing the polyol and amido functional cosolvents such that good print quality and fast dry times are achieved. Particular emphasis must also be placed on opaque ink jet receiver sheets, such as papers or white polyethylene terephthalate, where totally 10 different considerations exist than for ink jet transparencies employing a clear film base. There has been a drive in the ink jet industry to use paper as the base for the receiver sheet, as well as white or colored, opaque bases for graphics arts applications, so the need is imminent.

Accordingly, one objective of the present invention is to provide a novel opaque ink 15 jet receiver sheet, e.g., paper, containing a polyvinyl alcohol coating thereon, which receiver sheet is particularly applicable to the use of ink jet inks containing polyols having at least 3 hydroxy groups as cosolvents and/or amido functional compounds as cosolvents.

Another objective of the present invention is to provide a process for ink jet printing employing a receiver sheet in conjunction with inks containing polyols having at least 3 20 hydroxy groups and/or amido functional compounds as cosolvents. Still another object of the present invention is to provide a system for ink jet printing where the system employs the new generation inks containing polyols with at least 3 hydroxy groups and/or amido functional compounds as cosolvents.

These and other objectives of the present invention will become apparent upon a 25 review of the following specification and the claims appended thereto.

#### SUMMARY OF THE INVENTION

In accordance with the foregoing objectives, there is provided by the present invention an ink jet receiver sheet comprised of a substrate and a coating containing a modified 30 polyvinyl alcohol. The substrate is preferably opaque, e.g., paper based, and the modified polyvinyl alcohol is preferably carboxylated, acetoacetylated or modified with sulfonic acid. The polyvinyl alcohols modified in accordance with the present invention work very well with the newer class of ink jet inks that contain a polyol having at least 3 hydroxy groups

-5-

and/or an amido functional compound as a cosolvent. With the modified polyvinyl alcohol, the ink is found to spread upon contact with the surface. The use of a non-modified polyvinyl alcohol coated receiver sheet will not allow the ink to spread as easily, thereby causing ink coalescence or beading, and poor ink dry times.

- 5 In a preferred embodiment, hydrophilic resins such as polyvinyl pyrrolidone, polyacrylamide, and hydroxyethylcellulose may be added in minor amounts to the modified polyvinyl alcohol coating to aid in eliminating bronzing and to control dot size.

In another embodiment, there is provided a process for ink jet printing using an ink containing low levels of a polyol cosolvent having at least 3 hydroxy groups, preferably a  
10 triol, and/or an amido functional cosolvent in conjunction with an ink jet receiver sheet comprised of a modified polyvinyl alcohol coating, with the polyvinyl alcohol being carboxylated, acetoacetylated or sulfonated.

#### DETAILED DESCRIPTION OF THE INVENTION

- 15 The ink jet receiver sheet of the present invention includes a substrate. The substrate can be a clear film, an opaque film, or a paper. The clear films can be any of the conventional transparent resin films, generally thermoplastic films, such as polyester films, (e.g., polyethylene terephthalate), polystyrene, polyvinyl chloride, polymethylmethacrylate, cellulose acetate and the like. The opaque films can be comprised of white or colored film,  
20 such as polyethylene terephthalate. The opaque or colored films generally contain pigments, air bubbles or microbubbles in order to give the opaque appearance. Besides the white polyester film, other opaque films which can be used include vinyl films, preferably adhesive backed, which are available under the trademarks ScotchCal from 3M and RexCal from Rexham, Inc. The white polyester is commercially available, e.g., under the trademark  
25 Melinex from ICI-Films. Commercially available biaxially oriented polypropylene films, which are opaque, may also be used. The substrate can also be a paper based substrate. A photobase paper, which is a paper coated with polyethylene, provides a useful and preferred base for an ink jet receiver sheet.

- When a paper substrate is used, it is preferably sized. Sizing refers to water  
30 resistance, which is endowed to a cellulosic paper structure by hydrophobic internal or external treatments during paper making, such as the addition of rosin acids and starch. Typically, sizing is expressed in terms of the time taken for a given volume of a water-based liquid to penetrate the paper structure. The sized substrate is believed to enable minimized

-6-

penetration of the coating into the substrate paper, resulting in a distinct coating on the paper surface as opposed to a coating that has penetrated the paper fibers to a significant degree. Limited penetration of the coating into the substrate can permit one to realize certain advantages for color ink jet printing, such as providing a microscopically smooth surface  
5 affording symmetric spreading and negligible feathering of ink images, high and uniform optical density, high-color saturation, rapid ink absorption, and minimum inter-color bleed of juxtaposed solid areas. Such substrate papers are commercially available, e.g., from James River Corporation. The paper can also contain a commercially available filler.

The paper base can also be coated, with a photobase paper being a preferred substrate  
10 for the purposes of the present invention. Suitable photobase materials are commercially available. Such papers are generally coated with polyethylene, either high density or low density, or both, and can also contain gelatin subbing or anti-stat layers. One example of a suitable photobase material is that available from Glory Paper Mill of High Wycombe, U.K.

15 The coating of the present invention on the substrate is that of a modified polyvinyl alcohol. It is central to the present invention that the polyvinyl alcohol is modified, since the modification has been found advantageous whenever the new class of ink jet inks comprising a polyol and/or amido functional cosolvents is used. The polymer can be carboxylated, acetoacetylated or modified with sulfonic acid, e.g., sulfonated. Blends of the modified  
20 polyvinyl alcohol can be used, and a polyvinyl alcohol functionalized with more than one of the required functions can be used. It has been found that these modifications to the polyvinyl alcohol provide a polymer which when coated permits excellent results with the use of the new generation inks. No ink coalescence or beading is observed, and the ink dry times are excellent. As well, the print quality has been found to be quite good. The  
25 modified polyvinyl alcohol is the major component of the coating and generally comprises at least 50 weight percent of the solids in the coating, more preferably at least 70 weight percent, and most preferably at least 85 weight percent of the solids in the coating.

The modified polyvinyl alcohols useful in the practice of the present invention are available commercially. For example, Nippon Gohsei of Japan manufactures suitable  
30 carboxylated polyvinyl alcohols under the trademarks of GOHSENAL and GOHSESIZE. Acetoacetylated polyvinyl alcohols are available under the trademark GOHSEFIMER, and sulfonic acid modified polyvinyl alcohols are available under the trademark GOHSERAN.

Hydrophilic resins are preferably added to the polyvinyl alcohol coating in amounts of



-7-

anywhere from 0 to 30% based on the weight of the entire coating. It has been found that the presence of these hydrophilic resins aid elimination of bronzing and help to control dot size. Suitable hydrophilic resins include polyvinyl pyrrolidone, polyacrylamide and hydroxyethylcellulose.

5 Small amounts of surfactants for coatability and improved ink spreading, as well as a pigment for anti-blocking, may also be included in the coating. When a pigment is used, the amount of pigment is present in a very minor amount. Generally, the pigment to total polymer weight ratio in the coating is in a range of from about .001 to .1, more preferably in the range of .005 to .05 and most preferably in the range of .001 to .01.

10 The pigment can be any suitable inorganic pigment. Materials effectively used for this purpose are white or colorless porous inorganic pigments having an ionic property on the particle surface. Such pigments include natural zeolites, synthetic zeolites, diatomaceous earth, finely divided silica (average particle size up to 1 micron) with amorphous silica being preferred, powdered silica (average particle size up to 20 microns) and synthetic mica.

15 Other suitable pigment materials include calcium carbonate, magnesium carbonate, barium sulfate, titanium dioxide, magnesium titanate, calcium silicate, aluminum oxide or hydroxide and satin white. These pigments can be used, each alone or in mixture with one another.

Other suitable additives may also be incorporated into the coating. Such additives include thickeners, anti-oxidants, dye mordants, optical brighteners, all of which are well  
20 known to the art. These additives are added in any suitable functional amount.

Once the coating solution has been made, it can be coated upon the substrate using conventional methods. The coating can be applied, for example, by blade coating, knife coating, wire wound rod coating, roll coating, or any other suitable coating technique. A solution of water and coating composition can have any desired solids content, for example,  
25 from about 5 to about 25 weight percent. Different coating methods will have different optimal solids contents. The coating can be applied in any effective thickness or coating weight. The dry coating thickness can be of any desired value, with typical values being from about 5 to about 30 microns. Subsequent to coating, the receiver sheet can be dried by any suitable process, such as exposure to ambient air conditions, drying with a hot air dryer,  
30 a drum dryer, an oven, or the like.

The resulting ink jet receiver sheet exhibits excellent workability with the new generation class of ink jet inks that contain a polyol having at least 3 hydroxy groups as a cosolvent or an amido functional compound as a cosolvent. The polyol comprises a primary

-8-

carbon or carbon-oxygen chain which can be linear, branched or cyclic, and at least 3, i.e., 3 or more, hydroxy groups. Such preferred cosolvents include, for example, glycerol and 1,2,6-hexane triol. The amido functional cosolvents are those conventional solvents which contain an amido functionality, such as lactams. Among the most preferred solvents is pyrrolidone. Such polyol and amido functional cosolvents can be used alone, in mixture, or in mixture with other solvents, preferably alcohol solvents, such as polyethylene glycol or isopropanol.

The new generation of polyol and/or amido functional containing inks contain lower levels of the cosolvent, generally in the range of from about 1 to about 20 weight percent of the total solvent, and most preferably in the range of from about 4 to about 15 weight percent. The remainder of the solvent system generally comprises water. The colorants included in the ink are conventional.

The invention will be illustrated in greater detail by the following specific examples. It is understood that these examples are given by way of illustration and are not meant to limit the disclosure of the claims to follow. All percentages in the examples and elsewhere in the specification are by weight unless otherwise specified.

In the following examples, several components were used which are defined as follows:

SYLOID 620 is a 50 micron amorphous silica available from W.R. Grace.

GOHSENAL T-330H is a carboxylated polyvinyl alcohol available from Nippon Goshei of Japan.

PVP K90 is a polyvinylpyrrolidone resin with a K value of 90 available from International Specialty Polymers.

GAFQUAT 755 is a quaternized polyvinylpyrrolidone/dimethylaminomethyl-methacrylate copolymer available from International Specialty Polymers.

#### EXAMPLE 1

A mix was prepared with the following composition:

Distilled water - 8.97 grams

SYLOID 620 - 0.03 grams

10% GOHSENAL T-330H - 90 grams

PVP K - 90 - 1.00 grams

The composition was prepared by mixing the water and the SYLOID 620 in a container on a magnetic stirring plate for about 1 minute. The GOHSENAL T-330H solution and the PVP

-9-

K90 were then added, with stirring for an additional 30 minutes.

The composition was then coated onto a 400 gauge prebonded polyester base available from ICI under the trademark Melinex 582. The coating was accomplished with a No. 38 wire wound Meyer rod. The coating was placed in a laboratory blue M convection oven, and dried for 5 minutes at 220°F to obtain a coating thickness of about 9 microns.

The film was then printed on a Canon BJC820 ink jet printer using a full color square test pattern. The ink used with the Canon BJC820 printer contained a mixture of the cosolvents isopropanol, triethylene glycol and 1,2,6-hexanetriol in weight percent amounts of 2%, 6% and 6% respectively. The resulting print quality was good, with a very fast dry time, i.e., about 30 seconds at 50% RH, 22°C.

#### EXAMPLE 2

The following composition was prepared:

Distilled water - 4.97 grams

SYLOID 620 - 0.03 grams

15 10% GOHSENAL T-330H - 90 grams

20% GAFQUAT 755 - 5 grams

The composition was prepared by mixing the water and SYLOID 620 as described in Example 1. The GOHSENAL T-330H and GAFQUAT 755 were then added with stirring continuing for an additional 30 minutes. The composition was then coated and tested in the same manner as in Example 1.

The resulting print had very good ink dry time, with just slightly more ink coalescence than that observed with the composition in Example 1.

#### EXAMPLE 3

The coating composition of Example 1 was prepared and coated in the same manner onto a photobase paper available under the designation GS5081 from Glory Paper Mill, High Wycombe, U.K. The paper was printed using the Canon BJC820 ink jet printer with same ink as Example 1, and gave good print quality and a very fast dry time.

#### EXAMPLE 4

The coating composition of Example 1 was prepared except that an acetoacetylated polyvinyl alcohol (available under the trademark GOHSEFIMER Z200 from Nippon Gohsei of Japan) was substituted for the GOHSENAL T-330H in the same effective amount. The paper was printed using the Canon BJC820 ink jet printer with the same ink as Example 1, and gave good print quality and a very fast dry time.

-10-

EXAMPLE 5

The same formulation for the coating as prepared in Example 1 was used and coated in a similar manner onto Melinex 6110, a white opaque polyester film available from ICI Films, Hopewell, Va. The film was printed using the Canon BJC820 ink jet printer with the same ink as Example 1, and gave good print quality and a very fast dry time.

COMPARATIVE EXAMPLE

A commercial ink jet film utilizing a coating of a polyvinylpyrrolidone and styrenated acrylic resin was printed using the Canon BJC820 ink jet printer with the same ink as used in Example 5. The print quality was fair and the ink dry time was poor. This comparative example demonstrates the problems which occur when a conventional ink jet receiver sheet is used with the new generation inks.

EXAMPLE 6

The coating composition of Example 1 was prepared except that a sulfonated polyvinyl alcohol (available under the trademark GOHSERAN L3266 from Nippon Gohsei of Japan) was substituted for the GOHSENAL T-330H in the same effective amount. The film was printed using a Canon BJC820 ink jet printer with the same ink as Example 1 and gave good print quality and a very fast dry time.

EXAMPLE 7

The ink jet receiver sheets of Examples 1, 3 and 5 were printed using different ink jet printers and inks. The results are provided in the Table below. The results demonstrate that the best results are achieved when a new generation ink jet ink containing low levels of a cosolvent comprised of a polyol having at least 3 hydroxy groups or an amido functional compound such as pyrrolidone is used in combination with a receiver sheet coated in accordance with the present invention. When a more conventional ink containing a diol or especially a high percentage of diethylene glycol is used to print on the coated receiver sheet of the present invention, poorer results are obtained.

TABLE

Printer	Cosolvent	Cosolvent Percent	Example 1 (Clear Film)		Example 3 (Photobase Paper)		Example 5 (White Film)	
			Print Quality	Ink Dry Time	Print Quality	Ink Dry Time	Print Quality	Ink Dry Time
HP Paint Jet	diethylene glycol	60%	very poor	very poor	--	--	--	--
HP XL 300	diethylene glycol	8%	good	fair	good	fair	good	fair
Canon BIC820	isopropanol/tri- ethylene glycol/1,2,6- hexanetriol	2%/6%/6%	good	very good	good	very good	good	very good
Canon CJ-10	isopropanol/ glycerol/ triethylene glycol	2%/4%/4%	fair	very good	fair	very good	fair	very good
Iris Printer	glycerol	15%	very good	very good	very good	very good	very good	very good
Novajet	pyrrolidone	10%	--	--	very good	very good	very good	very good

**EXAMPLE 8**

The ink jet receiver sheet of Example 1 was printed with an HP Desk Jet (HP 500C) printer using an ink comprised of 8% pyrrolidone cosolvent, with the remainder of the solvent system in the ink being water, and a black colorant. In order to compare the print quality and dry time, the conventional ink receiver film designed for the HP Desk Jet printer, which comprises a coating of polyvinylpyrrolidone and styrenated acrylic resin, was also printed using the 8% pyrrolidone cosolvent ink. Both the image quality and dry time for the ink jet receiver sheet of the present invention (Example 1) were superior to that observed for the conventional ink receiver film.

The compatibility of the modified polyvinyl alcohol coated ink jet receiver sheet of the present invention with the new generation inks is quite demonstrative, even when an opaque base such as a paper base is used. Application of opaque bases such as paper in the graphic arts often requires a vibrancy and intensity of color with a clear sharp image. Due to the good print quality achievable when using the ink jet receiver sheet of the present invention in conjunction with the new inks, these requirements can be met for the new inks without sacrifice of more practical requirements such as good ink dry times.

While the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and the scope of the claims appended hereto.

-13-

WHAT IS CLAIMED:

1. An ink jet receiver sheet useful with inks containing a polyol cosolvent having at least 3 hydroxy groups or an amido functional cosolvent comprising

- 5           (i)     an opaque substrate, and  
          (ii)    a coating comprised of a polyvinyl alcohol which is carboxylated, acetoacetylated or sulfonated.

2. The ink jet receiver sheet of claim 1, wherein the substrate is comprised of a paper substrate.

10

3. The ink jet receiver sheet of claim 1, wherein the substrate is a white polyethyleneterephthalate substrate.

4. The ink jet receiver sheet of claim 1, wherein the substrate is comprised of photobase paper.

15

5. The ink jet receiver sheet of claim 1, wherein the coating further comprises less than 30 weight percent of a hydrophilic resin.

20           6. The ink jet receiver sheet of claim 5, wherein the hydrophilic resin is polyvinylpyrrolidone or copolymers thereof, polyacrylamide or an hydroxyethylcellulose.

7. The ink jet receiver sheet of claim 1, wherein the modified polyvinyl alcohol comprises at least 50 weight percent by solids of the coating.

25

8. The ink jet receiver sheet of claim 7, wherein the modified polyvinyl alcohol comprises at least 85 weight percent of the solids in the coating.

9. The ink jet receiver sheet of claim 1, wherein the polyvinyl alcohol is comprised of a blend of modified polyvinyl alcohols.

30

10. A process for generating images in an ink jet printing apparatus,

-14-

comprising incorporating the ink jet receiver sheet of claim 1 into said ink jet printing apparatus, and forming an image on the ink jet recording paper by causing ink comprised of a polyol cosolvent containing at least 3 hydroxy groups or an amido functional cosolvent to be expelled onto the coated surface.

5

11. The process of claim 10, wherein the ink is of different colors so that the image formed on the recording paper is a colored image.

12. The process of claim 10, wherein the ink jet receiver sheet incorporated into the ink jet printing apparatus has a coating comprised of the modified polyvinyl alcohol and a hydrophilic resin.

10

13. The process of claim 10, wherein the ink is comprised of glycerol or 1,2,6-hexanetriol.

15

14. The process of claim 10, wherein the ink is comprised of pyrrolidone.

15. The process of claim 10, wherein the cosolvent comprises from 1 to 20 weight percent of the ink.

20

16. A system for forming an image on an ink jet receiver sheet comprised of an ink jet printing apparatus and the ink jet receiver sheet of claim 1, with the ink being employed in the system being comprised of a cosolvent containing a polyol of at least 3 hydroxy groups or an amido functional compound.

25

17. The system of claim 16, wherein the ink jet receiver sheet has a coating comprised of polyvinyl alcohol and a hydrophilic resin.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/06815

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B41J 2/21; B41M 5/00; C09D 11/02

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/ 20R, 22R; 347/101; 427/152; 428/195, 211, 411.1, 480, 483, 500, 514, 520, 522, 535, 537.5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,220,347 (FUKUSHIMA et al) 15 June 1993, col. 2, lines 12-36.	10-17
Y	US, A, 5,017,223 (KOBAYASHI et al) 21 May 1991, col. 4, lines 23-39.	10-17
Y, P	US, A, 5,320,897 (KONDO et al) 14 June 1994, all.	1-17
Y	US, A, 4,624,985 (TSUTSUMI et al) 25 November 1986, col. 5, lines 5-27 .	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be part of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" documents referring to an oral disclosure, use, exhibition or other means

"T" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"A"

document member of the same patent family

Date of the actual completion of the international search

17 AUGUST 1994

Date of mailing of the international search report

12 SEP 1994

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

PAMELA R. SCHWARTZ

Telephone No. (703) 308-2351

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/06815

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

106/ 20R, 22R; 347/101; 427/152; 428/195, 211, 411.1, 480, 483, 500, 514, 520, 522, 535, 537.5